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(54) Title: SUPERPLASTIC TITANIUM BY VAPOR DEPOSITION

(57) Abstract

Methods are disclosed to render a wide range of titanium alloys superplastic at temperatures so low that oxidation is not a problem. Alpha beta alloys are vapor deposited to a particular microstructure which is superplastic. Alpha alloys and beta alloys are coevaporated with stabilizing particles.

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Description**SUPERPLASTIC TITANIUM BY VAPOR DEPOSITION****Technical Field**

This invention relates to superplastic titanium alloys and to the vapor deposition of titanium alloys.

Background Art

Titanium alloys are widely used in aerospace applications, especially for rotating parts in gas turbine engines. Titanium alloys have many attractive engineering properties which include useful mechanical properties such as strength, creep resistance and fatigue resistance over a wide temperature range, combined with low density and relatively good resistance to corrosion and oxidation at moderate temperatures. Unfortunately alloys of titanium are difficult to form and difficult to machine at high metal removal rates. These factors can raise the cost of many complex titanium structures to uneconomic levels.

Superplasticity is a useful, widely studied and complex phenomenon. Materials which exhibit superplastic behavior will exhibit neck-free plastic extensions of at least 100% measured in a one inch gage length tensile specimen when tested at a strain rate between 4×10^{-5} per second to 1×10^3 per second. Extensions of more than 150% are preferred. Materials which exhibit superplastic behavior can readily be formed into complex shapes, shapes which can eliminate the need for much machining. The subject of superplasticity is explained in the following technical publications which are incorporated herein by reference (see attached):

1. Hamilton & Ghosh, *Characterization of Superplastic Deformation Properties of Ti-6Al-4V*, TITANIUM 80 - SCIENCE AND TECHNOLOGY, H. Kimura and O. Izumi, eds., TMS-AIME, Warrendale, PA, 1980, pp. 1001-1014.

-2-

2. N. Furushiro et al., *Factors Influencing the Ductility of Superplastic Ti-6Al-4V Alloy*, in TITANIUM 80 - SCIENCE AND TECHNOLOGY, H. Kimura and O. Izumi, eds., TMS-AIME, Warrendale, PA, 1980, pp. 993-1000.
3. M.E. Rosenblum et al., *Microstructural Aspects of Superplastic Forming of Titanium Alloys*, in TITANIUM 80 - SCIENCE AND TECHNOLOGY, H. Kimura and O. Izumi, eds., TMS-AIME, Warrendale, PA, 1980, pp. 1015-1024.
4. I.I. Novikov and V.K. Portnoy, *Optimization of Heterogeneity as General Principal of Controlling Alloys Structure for Superplastic Forming*, in SUPERPLASTICITY AND SUPERPLASTIC FORMING, C.H. Hamilton and N.E. Paton, eds., The Minerals and Materials Society, Warrendale, PA, 1988, pp. 401-406.
5. N.E. Paton and C.H. Hamilton, *Microstructural Influences on Superplasticity in Ti-6Al-4V*, Metall. Trans A, vol. 10A, 1979, pp. 241-249.

Great effort has gone into the development of superplastic forming processes for titanium alloys. Many such processes exist and are widely used. See for example U.S. Patent No.: 4,886,559, U.S. Patent No.: 4,299,626, and U.S. Patent No.: 4,944,914. An apparent universal feature of prior art superplastic titanium processes has been the use of an elevated working temperature, usually about 980°F and invariable above about 890°F. The prior art processes are useful and are widely employed to form complex titanium articles. But, the prior art processes are still expensive. The common drawback to the prior art processes is the relatively elevated temperatures at which they must be performed. At elevated temperatures, above about 650°C to 760°C, and in the presence of oxygen, titanium is subject to rapid oxidation and rapid absorption of oxygen atoms into the lattice. Oxygen tends to embrittle titanium and is known to be a stabilizer of the alpha phase. Consequently, alpha plus beta titanium alloys, which are the most widely used class of

-3-

titanium alloys, are prone to the formation of a deleterious surface layer known as an alpha case when exposed to oxygen in temperatures in excess of about 650°C. This alpha case reduces the properties of titanium and generally must be removed physically or chemically prior to the use of such articles in service.

For this reason the prior art superplastic titanium forming processes which are performed at temperatures in excess of about 900°C are invariably performed in an inert or vacuum atmosphere. The requirement for such atmospheres adds substantial costs to the forming process not only in added equipment costs but in increased cycle times and costs for furnace atmospheres and the like. In addition, the oxidation of titanium alloys at these temperatures is still a common problem despite the use of inert atmospheres because of the difficulty of maintaining a sufficiently pure atmosphere.

Accordingly there exists a need for a method produce titanium alloys which can be superplastically formed at temperatures below which oxidation and oxygen contamination of titanium is a significant problem.

In this application, unless otherwise noted, compositions are presented to weight percent and phase and particle quantities are presented in volume percent.

Summary of the Invention

It is therefore the object of the present invention to describe a titanium material, and a method for producing such material, which can be superplastically formed at conditions below about 760°C and preferably below 650°C and which can therefore be superplastically formed at temperatures where oxidation is not a problem even in ambient atmospheres.

Superplasticity is a concept without an exact definition. Generally the term superplasticity refers to metallic material exhibiting tensile elongations much in excess of that which normally be observed. While for a normal metallic material a typical tensile stress might show an elongation of between 5% and 50%, superplastic material when tested at the appropriate elevated temperature can show an elongation of as much as 1500%. For the purpose of this disclosure, superplasticity will be defined as a elongation of

more than 100% and preferably more than 150% and most preferably be in excess of about 200 when measured in the temperature range of about 460°C to 560°C. Superplasticity has been the subject of great study for many years and many different observations and theories have resulted. It now seems that superplasticity results in large measure from grain boundary sliding, the movement of one grain relative to another in a direction lying in a plane which direction parallel to the plane separating the grains. Of course this grain boundary sliding must be accompanied by grain deformation to prevent the formation of voids or cavities. In titanium alloys it is known that grain boundary sliding along grain boundaries separating alpha grains is the most difficult to achieve. Grain boundary sliding along a boundary separating an alpha grain from a beta grain is the easiest type of deformation while boundaries sliding between two beta grains is intermediate between the previously described situations.

Consequently, the achievement of superplasticity in all alpha material is substantially more difficult than the achievement of superplasticity in material containing a mixture of alpha grains and beta grains. Achievement of superplasticity in all beta material has not been extensively studied but we believe it would be intermediate between the all alpha case and the alpha beta case.

Conventional superplastic titanium alloys are found to contain substantially equal volumes of the alpha and beta phase. It has been speculated that equal amounts of alpha and beta phases produce the ultimate possible degree of superplasticity. However, in accordance with the present invention, we have obtained 400% elongation in material containing 10% to 20% of the beta phase. This suggests the possibility that increasing the amount of the beta phase in materials made according to the present invention might further increase the degree of available superplasticity.

Because the superplasticity varies between the alpha/alpha situation, the alpha/beta situation and the beta/beta situation, the invention will be described first with respect to the alpha/beta situation which has been the most extensively studied and then with respect to the other conditions.

-5-

A major aspect of the invention is the method of making an extraordinarily fine grained titanium alloy through high-rate vacuum vapor deposition (e.g. at least 35 microns and preferably 50 microns to 100 microns per minute). The most commercially significant embodiment relates to alpha-beta titanium alloys such as 6% Al, 4% V bal Ti. The alloy composition and the vapor deposition parameters (substrate temperature) are selected so that the deposited fine grained alloy is in a non equilibrium condition containing more alpha phase than would be observed at equilibrium conditions. This excess alpha phase is metastable.

The result is a material which starts out being superplastic by virtue of its initial fine grain size and remains superplastic during deformation at elevated temperatures as a consequence of the transformation of the excess metastable alpha phase to beta phase at the boundaries between the original fine alpha grains. This beta precipitation between the original fine alpha grains effectively inhibits grain growth of the original alpha grains.

Consequently, titanium articles with this particular microstructure and processing history have the requisite properties to accomplish the above enumerated objects of the invention.

The initial fine grain size is accomplished by vacuum vapor deposition, preferably using an electron beam heat source. The evaporated titanium alloy vapor is collected on a cool substrate. As used herein cool is a relative term denoting that the substrate is cool relative to the temperature of the molten titanium vapor from which condensation is occurring. Substrate (deposition) temperature appears to be critical. Too high a temperature will result in an excessive grain size and too low a substrate temperature will result in a porous deposit. Condensation temperatures between about 500°C and 680°C are required.

The fine grained, partially metastable, titanium is removed from the substrate and deformed at temperatures between about 500°C and 535°C and when deformed under a strain rate of between about of at least about 1.7×10^{-3} and 1.7×10^{-4} , respectively, exhibits deformations in excess of 200%.

-6-

According to the invention the starting titanium composition must be an alpha beta alloy containing at least about 3% to 5% beta phase after vapor deposition and preferably at least about 10% to over 50% beta phase at the deformation temperature.

It is also possible to add insoluble particles such as borides and rare earth oxides.. Such particles can aid in preserving the fine grain size during deformation. As discussed below, such particles appear to be necessary in single phase alloys (all alpha or all beta) and optional in the case of alpha-beta alloys. The particle discussion below has equal applicability to alpha-beta alloys but is optional in such systems.

Brief Description of the Drawing

The Figure shows the relationship between the grain size and the temperature at which superplasticity is observed for conventional materials and materials according to the present invention.

Detailed Disclosure

We believe that alpha alloy behave as alpha alloys with as much as about 5% beta phase at the grain boundaries. At the other end of the range, near beta alloys can tolerate as much as 3% alpha at the grain boundaries before they behave as alpha beta alloys.

Alpha Plus Beta Titanium Alloys. According to the present invention, alloys containing from about 10% to over 50% volume beta at the superplastic forming temperature, are formed by vacuum vapor deposition on a substrate. The deposition process is performed under conditions which result in an extraordinarily fine grain size of less than about 2 microns and most preferably less than about 1 micron in the as deposited material as measured in a plane parallel to the substrate.

The vapor is evaporated from a molten pool of the titanium alloy or more rapidly from a hot pool of Nb, Ta, or W using a heat source such as an electron beam. U.S. Patent No.: 5,242,479 discusses an exemplary apparatus in the context of producing carbide coatings. This patent is incorporated by reference. The resultant vapor is condensed on a relatively cool substrate to form a homogeneous dense deposit having a columnar grain structure. The columnar grains have their long or columnar axis perpendicular to the

-7-

substrate and have a typical grain diameter in a plane parallel to the substrate of less than 2 microns and preferably less than 1 micron and have an aspect ratio, the ratio of the short diameter in a plane parallel to the substrate to the long dimension, in a plane perpendicular to the substrate, of from about 3 to 1 to about 100 to 1. Superplasticity inevitably requires a fine grain size. The present invention deposition process produces grains which meet the requirements for superplasticity in two dimensions, but not in a third dimension and superplasticity will initially be most apparent in planes containing the small dimensions of the grains. That is to say the full extent of superplasticity may not initially be observed when stress is applied in a direction parallel to the columnar axis of the grains. However, it is observed that after about 50% to 100% deformation the grains become equiaxed and thereupon display superplasticity in an isotropic fashion. We believe that the described columnar titanium structure is novel, useful, and non-obvious.

The particular techniques of physical vacuum vapor deposition do not appear to be critical to the success to the invention, so long as the essential microstructure is achieved. We have used apparatus such as that described in U.S. Patent No.: 5,242,479. The major advantage of the apparatus described in these patents is the high rate of deposition which can be achieved. This is however mainly a matter of economics rather than the properties of the resultant deposited material. Consequently, other forms of deposition appear possible. These include processes such as those depicted in U.S. Patent No.: 3,615,275 and U.S. Patent No.: 5,021,084, as well as other potential processes such as sputtering. Sputtering however is characterized by very low deposition rates rendering it unlikely to be an economical approach to the present invention. The apparatus in U.S. Patent No.: 5,242,479 is also desired because it can easily be adapted for co-evaporation to produce titanium materials containing particles.

It is important that the deposition be performed in a vacuum of at least 10^4 millimeters of mercury because of the high affinity of Ti for oxygen. In the work done to date the titanium vapor has been deposited on a substrate which is held about 20 centimeters above the molten titanium vapor source. The temperature of the substrate is critical to the successful performance of the present invention. If the substrate temperature is less than about 500°C the resultant deposits are porous and not useful. When the substrate deposition temperature is in excess of about 700°C the grain sized of the as

-8-

deposited material is greater than about 3 microns and the desired superplastic behavior at low temperatures is not observed. Only a narrow substrate (condensation) temperature range from about 500°C to about 680°C and preferably about 550°C to 650°C permits the deposition of titanium alloys satisfying the needs of the present invention for starting material. It should be noted here that the substrate temperatures are difficult to monitor. The substrate is located in the vapor cloud of titanium which is an extraordinarily reactive environment. This inhibits the use of direct surface contact instrument such as thermocouples. The titanium vapor cloud also interferes with optical perimetry. Consequently, we have measured the temperature at the back side of the substrate and using conventional thermodynamic calculations have been able to estimate closely the temperature of the front face of the substrate where the titanium is being deposited. During the deposition of thick layers of titanium the resistance to heat flow of the combined substrate and titanium coating increase as the coating thickness increases and we have compensated for this in our calculations. Other artisans who approach the practice of this invention using different equipment and different substrate materials and substrate geometries will necessarily have to devise their own methods for measuring and estimating the substrate surface temperature. It is clearly within the skill of one skilled in the art to practice the present invention merely by noting the substrate temperature at a place where such temperature can be conveniently measured and correlating the measured temperature with the characteristic grain size of the material deposited.

In our high rate deposition apparatus described in the papers mentioned above deposition rates on the order of 100 microns per minute have been achieved. These higher deposition rates resulted in increased heat flux to the substrate and require careful attention to substrate temperature. In our work to date we have used a monolithic substrate coated with a fluoride parting compound without specific provisions for cooling except such cooling as occurs by natural radiation. The parting agent appears to be optional. It is fully within the scope of this invention to employ auxiliary fluid cooling within the substrate or at the back face of the substrate to moderate and control substrate temperatures to achieve the desired objectives of the present invention.

As previously described the titanium alloy produced according to the invention has an initial fine grain size which permits low temperature superplastic forming. Under normal

-9-

circumstances in a typical titanium alloy such a fine grain structure would not persist at the deformation temperatures involved since rapid grain growth would occur, and once the grains grew to sizes much in excess of about 2 microns the superplastic behavior would be lost. What makes the present invention material unique is that as deposited it is in a metastable state because the vacuum vapor deposition process produces a high effective cooling rate. Such a high cooling rate suppresses the formation of the equilibrium quantity beta phase which would exist at the equilibrium. Upon heating to the deformation temperature this suppressed beta precipitates at the boundaries between the original alpha grains stabilizing such boundaries against motion associated with grain growth and thereby effectively preventing deleterious grain growth, while enhancing grain boundary sliding. This phenomenon permits extended superplasticity at the processing temperatures used permitting the forming of the alpha-beta alloy over a relatively long time period, permitting the forming of complex geometries and permitting the use of multiple deformation steps. At the conclusion of the deformation process the material can be heated to an elevated temperature sufficient to cause grain growth. Once the grains grow much above about 3 microns the lower-temperature superplastic effect is lost and the titanium thereupon exhibits the mechanical properties found in any other titanium alloy of similar composition and similar grain size. The alloy composition suitable for use in the present process can be described as alpha plus beta alloys which have an equilibrium beta content of at least about 10% at the intended deformation temperature. TABLE I below lists a variety of alloys which can be satisfactorily processed according to the present invention.

-10-

TABLE I	
Alpha Beta Alloys (wt%)	Ti-6Al-4V Ti-6Al-25n-42r-2Mo Ti-5Al-2.55n
Beta Alloys	Ti-15V-3Cr-3Sn-3Al
Alpha Alloys	Commercially Pure Ti

We have worked almost exclusively with an alloy based upon the common titanium alloy whose nominal composition is 6% aluminum 4% vanadium balance titanium. Experimental equipment deficits generally resulted in the deposition of an alloy containing more vanadium than aluminum. Nonetheless the resultant alloy contains necessary beta phase and exhibited the superplasticity which is the essence of the invention.

All Alpha and All Beta Alloys. The previously described alpha-beta alloys such as Ti -6%, Al 4% V achieve and maintain superplasticity, in the practice of the invention, primarily through the metastable alpha to beta transformation mentioned above. Such a mechanism cannot be operative when the titanium material is not metastable but is especially single phase (either all alpha or all beta) at the deformation temperature.

We have achieved useful superplasticity in such non-metastable, single phase materials by adding a fine precipitate distribution to stabilize the grain size during superplastic deformation. The starting grain size in such systems is achieved by the same vapor deposition techniques (and substrate temperature control) as discussed with respect to alpha-beta alloys.

Principally we have developed and successfully employed a titanium mono-boride particle distribution. We have also employed rare earth oxides as stabilizing particles.

To produce TiB particle distribution it is necessary to supply a source of boron and to co-evaporate boron along with the titanium material. We use an apparatus like that shown in U.S. Patent No.: 5,242,479 and adjust the relative evaporation rates so as to produce up to 15.0% by volume of TiB particles in the deposited layer, preferably 0.5% to

-11-

5.0% by volume. TiB is extremely stable and insoluble in titanium and the resultant particles have average diameters of less than about 200°A (preferably less than 150°A) and average inter-particle spacings of less than about 2,000°A (preferably less than 1,000°A). The particle size and spacing are affected by the substrate temperature and deposition rate. For boron sources we have used Z_xB₂ (the resultant Z_x level in the material is not a problem) but are confident that other compounds such as TiB, TiB₂, B and the borides of Aluminum and Vanadium could be used.

We have also employed rare earth oxides such as those based on the group 3b elements in the Periodic Table and the Lanthanides and especially we have used _____.

The development of rare earth dispersions exactly parallel the previously-mentioned preparation of TiB dispersion. The source may be either the rare earth oxide or simply the pure rare earth. If the pure rare earth is employed, it will be found that sufficient oxygen will be present as an impurity to fully oxidize the rare earth.

It is also possible to us both TiB and rare earth oxide particles in a single material by using a triple co-evaporation scheme. TiB is usually preferred because it is more stable than the rare earth oxides.

Although the invention has been shown and described with respect to preferred embodiments and application to certain titanium alloys, it should be evident to those skilled in the art that it is applicable to a wide variety of titanium alloys and that various changes made therein without departing from the spirit and scope of the invention.

-12-

Claims:

- 1 1. A method for producing a titanium material which exhibits superplastic properties
2 at temperatures below about 760°C including the steps of:
3
4 a. co-evaporating a titanium alloy and a material selected from the group
5 consisting of sources, a rare earths, rare earth compounds and a rare earth
6 alloys and mixtures thereof, in a vacuum environment, at relative rates so
7 that the titanium alloy comprises at least about 85% volume of the total
8 evaporated material;
9
10 b. condensing the co-evaporated material onto a substrate maintained at a
11 temperature of between about 500°C and 680°C,
12
13 Whereby the resultant condensed material contains a dispersion of particles selected
14 from the group consisting of TiB and rare earth oxides and mixtures thereof, said
15 particles having average diameters of less than about 200° and average inter-
16 particle spacings of less than about 1,000°, and has a grain size of less than about 2
17 microns in a plane parallel to the substrate.
18
1 2. The method of producing a titanium alloy material containing a fine dispersion of
2 TiB particles comprising the step of:
3
4 co-evaporating the titanium alloy material and a source of boron in a
5 vacuum environment condensing said evaporated material onto a cooled
6 substrate held at a temperature of 500°C to 680°C
7
1 3. A method of superplastically forming a titanium alloy at a temperature below about
2 760°C, including the steps of:
3
4 a. providing a starting titanium alloy material having an average grain size of
5 less than about 2 microns when measured in at least one plane, and having a
6 metastable alpha rich microstructure,

-13-

7 b. deforming said metastable material at a temperature of ____ to ____ and at
8 a strain rate of 10^{-5} to 10^{-3} per second,

9

10 whereby, during deformation said metastable alpha phase transforms in part to the
11 beta phase and forms said beta phase at the grain boundaries between the original
12 fine alpha grains thereby stabilizing the original alpha grain size against significant
13 grain growth and providing a large alpha-beta grain boundary area to permit grain
14 boundary slip during deformation.

15

1 4. A method as in claim 3 wherein the starting material contains a fine dispersion of
2 stable particles.

3

1 5. A method as in claim 4 wherein said stable particles are essentially TiB.

2

1 6. A titanium material, said material:

2

3 a. having an average grain size of less than about 2 microns measured in at
4 least one plane and consisting in part of metastable alpha phase;

5

6 b. exhibiting a tensile elongation in excess of about 150% when tested a
7 temperature of less than about 650°C when the major stress axis essentially
8 lies in a plane in which the measured grain diameter is less than about 2
9 microns.

10

1 7. A titanium material, said material:

2

3 a. having an average grain size of less than about 2 microns measured in at
4 least one plane and consisting in part of metastable alpha phase containing
5 up to 2.5 volume of finely dispersed stable particles;

6

7 b. exhibiting a tensile elongation in excess of about 150 when tested a
8 temperature of less than about 650°C when the major stress axis essentially

-14-

9 lies in a plane in which the measured grain diameter is less than about 2
10 microns.

-15-

- 1 8. A titanium material as in claim 7 wherein the particles have an average diameter of
2 less than about 200° and an average inter-particle spacing of less than about 1,000°.
3
- 1 9. A titanium material as in claim 7 wherein the particles are selected from the group
2 consisting of TiB and rare earth oxides and mixtures thereof.
3
- 1 10. A titanium material as in claim 7 wherein the particles are essentially TiB.
2
- 1 11. A titanium material as in claim 7 wherein the particles are essentially rare earth
2 oxides.
3
- 1 12. A titanium material, said material:
2
 - 3 a. having an average grain size of less than about 2 microns measured in at
4 least one plane and consisting essentially of alpha grains containing 0.5%
5 volume to 2.5% volume of finely dispersed stable particles;
6
 - 7 b. exhibiting a tensile elongation in excess of about 150 when tested a
8 temperature of less than about 650°C when the major stress axis essentially
9 lies in a plane in which the measured grain diameter is less than about 2
10 microns.
11
- 1 13. A titanium material as in claim 12 wherein the particles have an average diameter of
2 less than about 200° and an average inter-particle spacing of less than about 1,000°.
3
- 1 14. A titanium material as in claim 12 wherein the particles are selected from the group
2 consisting of TiB and rare earth oxides and mixtures thereof.
3
- 1 15. A titanium material as in claim 12 wherein the particles are essentially TiB.
2
- 1 16. A titanium material as in claim 12 wherein the particles are essentially rare earth
2 oxides.

-16-

1 17. A titanium material, said material:

2

3 a. having an average grain size of less than about 2 microns measured in at
4 least one plane and consisting essentially of beta grains containing 0.5%
5 volume to 2.5% volume of finely dispersed stable particles;

6

7 b. exhibiting a tensile elongation in excess of about 150 when tested a
8 temperature of less than about 650°C when the major stress axis essentially
9 lies in a plane in which the measured grain diameter is less than about 2
10 microns.

11

1 18. A titanium material as in claim 17 wherein the particles have an average diameter of
2 less than about 200° and an average inter-particle spacing of less than about 1,000°.

3

1 19. A titanium material as in claim 17 wherein the particles are selected from the group
2 consisting of TiB and rare earth oxides and mixtures thereof.

3

1 20. A titanium material as in claim 17 wherein the particles are essentially TiB.

2

1 21. A titanium material as in claim 17 wherein the particles are essentially rare earth
2 oxides.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US 94/12807

A. CLASSIFICATION OF SUBJECT MATTER

C 23 C 14/22, C 22 C 14/00, C 23 C 14/14, C 23 C 14/30

According to International Patent Classification (IPC) or to both national classification and IPC 6

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C 23 C, C 22 C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SUPERPLASTICITY AND SUPERPLASTIC FORMING, The Minerals, Metals and Materials Society, issued 1988 I.I. NOVIKOV et al. "Opti- mization of Heterogeneity as General Principle of Controlling Alloys Structure for Superplastic Forming", pages 401-406 (cited in the application). --	1-21
A	US, A, 4 299 626 (NEIL E. PATON et al.) 10 November 1981 (10.11.81), abstract; claims 1-2 (cited in the application).	1-21

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

-2-

International Application No
PCT/US 94/12807

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 5 242 479 (BORIS A. MOVCHAN et al.) 07 September 1993 (07.09.93), abstract; fig. 1; claims 1-12 (cited in the application). --	1-21
A	US, A, 5 021 084 (LEONARD M. BIANCHI) 04 June 1991 (04.06.91), abstract; fig.; claims 1-7 (cited in the application). --	1-21
A	GB, A, 2 224 040 (MINNESOTA MINING AND MANUFACTURING COMPANY) 25 April 1990 (25.04.90), abstract; claims 1-23. ----	1-21

ANHANG

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ANNEX

to the International Search
Report to the International Patent
Application No.

ANNEXE

au rapport de recherche inter-
national relatif à la demande de brevet
international n°

PCT/US 94/12807 SAE 100631

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